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# The effects of thermal load and frost cycles on the water transport in two high-performance concretes

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## Abstract

Moisture diffusivity of two high-performance concretes used in concrete containment buildings of nuclear power plants is measured as a function of temperature up to  $80^{\circ}$ C, and the effects of high-temperature exposure up to  $800^{\circ}$ C and freeze/thaw cycles on its value are analyzed. The temperatures in the range of  $0-80^{\circ}$ C are found to have a moderate effect on the moisture diffusivities of both concretes, the typical increase being about 100-200% over the whole region. The high temperature exposure results in a much more significant increase of moisture diffusivity, up to three orders of magnitude, and the freeze/thaw exposure of 400 cycles to an increase up to one order of magnitude. As the main reason for the mentioned moisture diffusivity increase, the crack formation is identified. Both thermal decomposition accompanied by release of substantial amount of gaseous substances and water freezing in the porous system can damage the internal microstructure of the matrix due to the significant pressure increase in the porous body. The magnitude of changes of moisture diffusivity is found to be affected by the quality of aggregates rather than by the quality of cement. High quality quartzitic aggregates with very low porosity and very good mechanical properties perform much better than other more porous siliceous aggregates such as opal, and than the calcareous aggregates such as chalk. © 2001 Elsevier Science Ltd. All rights reserved.

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# 1. Introduction

Transport processes of water in concrete can be described basically by two different treatments. The first one utilizes the analogy to water transport in soils and employs the hydraulic conductivity K (in m/s) defined by Darcy's law (Eq. (1)) [1]

$$v = -K \text{ grad } h, \tag{1}$$

where v is the average velocity of water in porous medium, v = Q/A, Q is the rate of flow of water (in m<sup>3</sup>/s), A is the cross-sectional area of the porous medium, h is the hydraulic head in meters.

This description is employed by most of the researchers specializing in the testing of concrete (see e.g., Refs.

[2-6]). The coefficient of hydraulic conductivity is denoted here "water permeability," which is probably a matter of tradition.

An alternative treatment that is preferred by the researchers working in the field of building physics (see e.g., Refs. [7–11]) uses the moisture diffusivity  $\kappa$  (in m<sup>2</sup>/s) as the main phenomenological coefficient (Eq. (2)),

$$j = -\kappa \operatorname{grad} \rho_{\mathrm{m}},\tag{2}$$

where *j* is the water flux (in kg/m<sup>2</sup>s),  $\rho_m$  is the partial density of moisture in a porous material which can be expressed using either moisture content by mass *u*,  $\rho_m = \rho_s u$ ,  $\rho_s$  is the partial density of the porous matrix, or moisture content by volume *w*,  $\rho_m = \rho_w w$ ,  $\rho_w$  is the density of water.

As for the quality of description of water transport in porous media, the two aforementioned treatments are practically equivalent, although both soil physicists and building physicists restrict themselves for one of them in most cases. However, it looks again more or less like a matter of tradition.

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In any case, the phenomenological coefficients are convertible between each other as it has been shown already by Philip and de Vries [12].

In isothermal conditions, a simple relation between *K* and  $\kappa$  can be derived taking into account that (Eq. (3))

$$j = \rho_{\rm w} v. \tag{3}$$

Commonly used assumptions (Eqs. (4) and (5))

 $\rho_{\rm s}={\rm constant}, \qquad (4)$ 

 $\rho_{\rm w} = {\rm constant}$ (5)

lead to the following conversion formulas (Eqs. (6) and (7))

$$\kappa = K \frac{\rho_{\rm w}}{\rho_{\rm s}} \frac{\partial h}{\partial u},\tag{6}$$

$$\kappa = K \frac{\partial h}{\partial w},\tag{7}$$

where  $\partial h/\partial u$ ,  $\partial h/\partial w$  can be obtained from the water retention curves h = h(u) or h = h(w), respectively.

In this paper, we follow the second treatment. In our experimental work, the moisture diffusivity is measured as a function of temperature up to  $80^{\circ}$ C, the effect of high-temperature- and frost-cycles exposure on its value is also analyzed.

#### 2. Method for measuring the moisture diffusivity

Most of the methods for determining moisture diffusivity are based on the analysis of measured moisture profiles (see e.g., Refs. [13-16]). This might be a very time consuming task for materials with low moisture diffusivity such as concrete where water penetration to a depth of only a couple of centimeters can take several weeks or months depending on the type of the mixture.

Therefore, we employed the PCK method that we commonly use for the determination of moisture diffusivity of plate materials (see Ref. [17]). The overall accuracy of the method was analyzed recently on a homogeneous material, namely the extruded porcelain mixture containing kaolin, clay, feldspar and Al<sub>2</sub>O<sub>3</sub> [18]. The moisture diffusivity was determined using the measured moisture profiles in suction experiments by the well-known Boltzmann-Matano analysis [13] and by the double-integration method [16], and compared with the results obtained using the simple method from Ref. [17]. The differences in calculated moisture diffusivities were lower than 50% in the range of higher moistures (for lower moisture content the method is not suitable for practical applications), which can be considered as reasonable taking into account the simplicity of the method. The PCK method was also tested on two cementitious fiber composites [18]. Even for these nonhomogeneous materials the maximum differences from the Matano treatment were in the range of 60-80%. For the first view, this accuracy might not be considered as very high but the process of solving inverse problems of moisture transport is very difficult and highly sensitive to input errors. As it has been shown in the computational analysis by Černý et al. [19], the deviations as high as 20-30% from the correct value of moisture diffusivity can already be considered as a very good result. The PCK method was already employed for measuring moisture diffusivity of a high-performance concrete in the past [20].

The PCK method consists in the assumption that the moisture diffusivity  $\kappa$  can be considered as piecewise constant with respect to the moisture content. As Ref. [17] may not be directly accessible for all readers, we will describe some mathematical and experimental details of the method in what follows.

The experimental setup of the PCK method is identical with that of a common suction experiment. The specimens having the form of a plate or a prism are water- and vaporproof insulated on all lateral sides, i.e., the sides parallel to the main direction of water transport. This can be done, for instance, by an epoxy resin. Then, the specimens are put on a viscous sponge and suck water from a free water surface (see Fig. 1). The mass of the specimens is determined as a function of time, in the simplest case just by interrupting shortly the experiment in the chosen time intervals and weighing the specimen. In this way, the amount of water in the specimen as a function of time is determined. The mathematical analysis of the above problem is as follows.

Due to the chosen geometry of the experiment, the problem of moisture transport can be reduced to only one dimension. Thus, we can write in certain (not very wide) range of moisture the transport equation in the form

$$\frac{\partial \rho_{\rm m}}{\partial t} = \kappa \frac{\partial^2 \rho_{\rm m}}{\partial x^2}.$$
(8)



Fig. 1. Experimental setup for measuring the moisture diffusivity.

The initial and boundary conditions can be defined as

$$\rho_{\rm m}(x,0) = \rho_2,\tag{9}$$

$$\rho_{\rm m}(0,t) = \rho_1,\tag{10}$$

$$\rho_{\rm m}(d,t) = \rho_2 \tag{11}$$

where  $\rho_2$  is the initial partial moisture density in the specimen,  $\rho_1$  is the maximum partial moisture density (water saturation value) that can be achieved in the material (we suppose that the bottom surface of the specimen is in direct contact with water during the water suction process), *d* is the thickness of the specimen in the direction of water flow.

The diffusion problem (Eqs. (8)-(11)) can be solved analytically with the result:

$$\rho_{\rm m}(x,t) = \rho_1 + (\rho_2 - \rho_1) \frac{x}{d} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{\rho_2 - \rho_1}{n} \sin\left(\frac{n\pi x}{d}\right) \exp\left(-\frac{\kappa n^2 \pi^2 t}{d^2}\right).$$
(12)

The total mass of water that penetrated into the specimen during the time interval  $[0,\tau]$  can be expressed by the relation

$$m_{\rm m}(\tau) = S \int_{0}^{d} (\rho_{\rm m}(x,\tau) - \rho_2) \mathrm{d}x.$$
 (13)

After substituting Eq. (12) into Eq. (13) we get the final transcendent equation for  $\kappa$ 

$$m_{\rm m}(\tau) - S(\rho_1 - \rho_2) \frac{d}{2} + \frac{2dS}{\pi^2} (\rho_1 - \rho_2) \sum_{n=1}^{\infty} \frac{1}{n^2} \times (1 - \cos(n\pi)) \exp\left(-\frac{\kappa n^2 \pi^2 \tau}{d^2}\right) = 0,$$
(14)

which can be solved by some of the iterative methods, such as the Newton method. The value of  $\kappa$  determined by the solution of Eq. (14) we award to a characteristic average value of the partial moisture density in the time interval  $[0,\tau]$ ,

$$\rho_{\rm m,c} = \frac{m_{\rm m}(\tau)}{2Sd} + \frac{\rho_2 + \rho_1}{2}.$$
 (15)

In practical measurements we perform the experiment with a set of specimens with various values of the initial partial moisture density  $\rho_2$ , and determine the corresponding set of values of the moisture diffusivity  $\kappa(\rho_{m,c})$ . In this way we obtain a pointwise given  $\kappa(\rho_m)$  function, i.e., the dependence of the moisture diffusivity on the partial moisture density.

### 3. Materials and specimens

Experimental work was done with two types of high-performance concretes designed for nuclear safety-related structures.

The Penly concrete was used for a concrete containment building in a nuclear power plant in France, and consisted of the following components: Cement CPA 52.5 HP Le Havre (290 kg m<sup>-3</sup>), mostly siliceous aggregates: 0/5 size fraction (831 kg m<sup>-3</sup>), 5/12.5 size fraction (287 kg m<sup>-3</sup>), and 12.5/25 size fraction (752 kg m<sup>-3</sup>), calcareous filler PIKETTY (105 kg m<sup>-3</sup>), silica fume (30 kg m<sup>-3</sup>), water (131 kg m<sup>-3</sup>), retarder CHRYTARD 1.7, superplasticizer Rèsine GT 10.62.

The Temelin concrete was used for the concrete containment building of the Temelin nuclear power plant in the Czech Republic. The composition was the following: Cement 42.5 R Mokrá (499 kg m<sup>-3</sup>), fully quartzitic aggregates: sand 0/4 size fraction (705 kg m<sup>-3</sup>), gravel sand 8/16 size fraction (460 kg m<sup>-3</sup>), and gravel sand 16/22 size fraction (527 kg m<sup>-3</sup>), water (215 kg m<sup>-3</sup>), plasticizer 4.5 l m<sup>-3</sup>.

The specimens had prismatic shape,  $100 \times 100 \times 50$  mm, and before the measurements of moisture diffusivity they were exposed to various external conditions.

The first group of the specimens (supposed to be applied for the measurements of  $\kappa$  dependence on temperature up to 80°C) was left in laboratory conditions and the moisture diffusivity measurements were done 6 months after the production of specimens. The second group was exposed to thermal load. This group of specimen was further divided into four subgroups. Each subgroup was exposed to a predetermined temperature in a furnace. The chosen temperatures were 200°C, 400°C, 600°C, and 800°C. The initial moisture content of the specimens was equal to the equilibrium moisture content in the laboratory. The heating period from room temperature to the predetermined temperature was 60 min, the specimens remained at the predetermined temperature another 60 min, and then they were slowly cooled so that it took about 6-8 h to get to the room temperature conditions again. Measurements of moisture diffusivity were done 6 months after specimens production. The third group of the specimens was exposed to several hundreds of frost cycles according to the Czech standard ČSN 731322 just after the 28-day curing period. One frost cycle consisted in freezing to  $-20^{\circ}$ C for 4 h and subsequent thawing at  $+20^{\circ}$ C for 2 h. In the thawing part of the cycle, a state close to 100% relative humidity was kept in the conditioning chamber. Measurements of moisture diffusivity were done again 6 months after the end of the frost cycling procedure. The final, fourth group of the specimens was employed as a reference for the frost-exposed materials. They were kept at room temperature in water for the whole time of the cycling procedure (about 10 months), then they were left for an additional 6 months on the air in laboratory conditions before measurements of moisture diffusivity.

Always three specimens exposed to the same conditions were employed for every particular measurement of moisture diffusivity.

#### 4. Experimental results

For the determination of moisture diffusivity, the  $50 \times 100$  mm sides of the specimens were water- and vapor-proof insulated by the resin Chs-Epoxy 1200 in order to secure the one-dimensional water transport. The experiment was performed in the way shown in Section 2. One



Fig. 2. Results of suction experiments on (a) Penly concrete and (b) Temelin concrete performed at constant temperatures in the range of  $T \in [5^{\circ}C, 80^{\circ}C]$ .

Table I					
(a) Water absorption coeffic depending on temperature in	cients o the ran	f Penly ge of $T \in  $	concrete [5°C, 80°	in kg m C]	-2 s <sup>-1/2</sup>
Heating temperature [°C]	5	25	40	60	80
Water absorption coefficient	0.0101	0.0111	0.0103	0.0104	0.0126
(b) Water absorption coeffici depending on temperature in	ents of the ran	Temelin c ge of <i>T</i> ∈∣	concrete i [5°C, 80°	n kg m <sup>-</sup> C]	<sup>2</sup> s <sup>-1/2</sup>
Heating temperature [°C]	5	25	40	60	80
Water absorption coefficient	0.016	0.021	0.022	0.024	0.028

part of the experimental work was carried out in a conditioning chamber to expose the specimens to elevated temperatures, another part was done in room temperature conditions in a laboratory where stable temperature conditions  $T=25.0\pm1.0^{\circ}$ C were kept. The mass of the specimens was recorded in 10-s intervals. The moisture diffusivity was determined as an average value from three or four measurements on every specimen. For the sake of comparison with suction experiments performed by other authors, we calculated also the values of the water absorption coefficient A, defined as Eq. (16)

$$i = A\sqrt{t},\tag{16}$$

where *i* is the cumulative water absorption measured in kg/m<sup>2</sup>, *t* is the time from the beginning of the suction experiment.

As our experiments had a comparative character only, we did not determine the whole  $\kappa(u)$  functions but measured  $\kappa$  for just one characteristic value of the moisture content. The initial state for moisture diffusivity measurements was the dry material, the drying was performed in a dryer at the



Fig. 3. Dependence of moisture diffusivity of Penly concrete and Temelin concrete on temperature for  $T \in [5^{\circ}C, 80^{\circ}C]$ .

temperature 110°C. Therefore, according to Eq. (15), the characteristic average values of moisture content were  $u \sim 3\%$  kg/kg for Penly concrete and  $u \sim 4.5\%$  kg/kg for Temelin concrete. This decision was also supported by our previous experience with another type of concrete where for instance longer water exposure (necessary to achieve higher initial moisture values) after thermal loading has often led to a destruction of some specimens.

In the first part of our experimental work the dependence of moisture diffusivity on temperature was determined. Only the temperature range of  $5-80^{\circ}$ C was considered because



Fig. 4. Results of suction experiments on (a) Penly concrete and (b) Temelin concrete depending on the heating temperature.

Table 2	2
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(a) Water absorption coeffic depending on heating temper	cients o rature	f Penly o	concrete	in kg m	- 2 s - 1/2
Heating temperature [°C]	25	200	400	600	800
Water absorption coefficient	0.011	0.012	0.029	0.914	1.320
(b) Water absorption coeffici depending on heating temper	ents of ' rature	Temelin c	oncrete in	n kg m <sup>-2</sup>	<sup>2</sup> s <sup>-1/2</sup>
Heating temperature [°C]	25	200	400	600	800
Water absorption coefficient	0.021	0.022	0.064	0.158	0.329

for lower temperatures the effect of ice formation and for higher temperatures that of water vapor production affect the liquid moisture transfer in a significant way, so that the moisture diffusivity would also include other phases. The specimens together with the vessel with water were first conditioned in a climatizing chamber at the predetermined temperatures, which were chosen as 5°C, 25°C, 40°C, 60°C, and 80°C, for the time period of 2 h. Then, the specimens were put on the sponge in the vessel, and the suction experiments were started.

The results of suction experiments are shown in Fig. 2a,b. The calculated values of the water absorption coefficient are in Table 1a,b, the moisture diffusivities in Fig. 3. Apparently, the water absorption coefficient and the moisture diffusivity of both materials increase with temperature, and this increase is more significant for the Temelin concrete than for the Penly concrete. The values of  $\kappa$  for Temelin concrete are approximately two times higher compared to Penly concrete, and about the same ratio have the water absorption coefficients of both materials.

In the second part of the experiments, the effect of high temperature exposure was studied. The measurements were



Fig. 5. Dependence of moisture diffusivity of Penly concrete and Temelin concrete on heating temperature.



Fig. 6. Results of suction experiments on (a) Penly concrete and (b) Temelin concrete depending on the number of frost cycles.

done at room temperature,  $T = (25.0 \pm 1.0)^{\circ}$ C. The results are summarized in Fig. 4a,b and Table 2a,b (suction experiments), and Fig. 5 (moisture diffusivities). It is apparent that the moisture diffusivity of both materials increases with the heating temperature very fast. An interesting feature can be observed. While in the temperature range up to 400°C the moisture diffusivity of Penly concrete remains approximately two times lower than of Temelin concrete similarly as at room temperature, for temperatures 600°C and higher the situation is changed dramatically, and Penly concrete has more than one order of magnitude higher moisture diffusivity than Temelin concrete.

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ab	le	3	

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(in kg m <sup><math>-2</math></sup> s <sup><math>-1/2</math></sup> ) of Penly co	ncrete		ipuon coonicion
Number of frost cycles	0	200	300
Water absorption coefficient	0.016	0.065	0.084
(b) Effect of the number of fros (in kg m <sup>-2</sup> s <sup>-1/2</sup> ) of Temelin	st cycles on	the water abso	orption coefficien

Number of frost cycles	0	200	300
Water absorption coefficient	0.031	0.044	0.064

In the third and final part of the experimental work, the effect of frost cycles on moisture diffusivity was studied. The results are shown in Fig. 6a,b and Table 3a,b (suction experiments), and Fig. 7 (moisture diffusivities). We can observe that for specimens not exposed to frost cycles, Penly concrete has again about two times lower moisture diffusivity than Temelin concrete. However, while the moisture diffusivity of Temelin concrete increases only slowly with the number of frost cycles, approximately one-half order of magnitude after 400 cycles, the moisture diffusivity of Penly concrete increases much faster, after 50 cycles it is already higher than the moisture diffusivity of Temelin concrete, and after 200 cycles it is about one order of magnitude higher compared to the reference specimens.

# 5. Discussion

The generally lower value of moisture diffusivity of Penly concrete than of Temelin concrete in usual conditions is apparently related to its lower porosity. The saturation



Fig. 7. Dependence of moisture diffusivity of Penly concrete and Temelin concrete on the number of frost cycles.

moisture content for Penly concrete is 4.8% kg/kg, and for Temelin concrete 7.0% kg/kg.

The dependence of moisture diffusivity on temperature can be expressed by an approximate relation [21]

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$$\frac{\kappa(T)}{\kappa(T_0)} = \frac{\left(\frac{\sigma}{\eta}\right)_T}{\left(\frac{\sigma}{\eta}\right)_{T_0}},\tag{17}$$

where T is the actual temperature,  $T_0$  a reference temperature,  $\sigma$  is the surface tension of water,  $\eta$  is the viscosity of water. We have taken  $T_0 = 25^{\circ}$ C and calculated the theoretical  $\kappa(u)$  functions for both materials. The results in Fig. 3 show that our measured data gave flatter curves than those calculated from formula (17). A better agreement was achieved for Temelin concrete than for Penly concrete. The differences between the theoretical and experimental values cannot be fully assigned to experimental errors although they are relatively high for this simple method, about 20% according to our error analysis. The different character of theoretical and experimental  $\kappa(T)$  curves, namely the significant differences in their second derivatives, will probably be also due to the approximate character of formula (17), which takes into account water only and not its interaction with the porous matrix.

The very fast increase of moisture diffusivity of both materials with the heating temperature (Fig. 5) corresponds to the theoretical predictions of the effects of high temperatures on concrete in general. From the point of view of structural changes, for the temperature range up to 1000°C two processes are the most important, namely the decomposition of Ca(OH)<sub>2</sub> at about 460°C and the decomposition of calcium silicate hydrates at about 700°C (see e.g., Ref. [3]). During these processes, gaseous substances are released, water vapor in the first case, and carbon dioxide in the second. Therefore, the amount of bigger pores increases, which makes the liquid water transport easier and faster. In addition, due to the fast generation of a substantial amount of the mentioned gaseous substances, the local overpressure in some parts of the porous system may lead to crack appearance, and consequently to the opening of preferential paths for the pore water flow.

The increase in moisture diffusivity of Penly concrete between 400°C and 800°C (Fig. 5) was much faster than for Temelin concrete. This is most probably a consequence of the opening of wider preferential paths after the high temperature exposure because in normal conditions Penly concrete possesses lower moisture diffusivity than Temelin concrete.

First supporting arguments to this hypothesis can be found in Table 4a. We can see a dramatic increase in the saturation moisture content (i.e., in the content of open pores) of Penly concrete between 400°C and 600°C (more than 30%) while for Temelin concrete we found only an about 20% increase (Table 4b). As Penly concrete contains a significantly lower amount of cement than Temelin

Table 4	4
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(a) Effect of heating temperatu	re on the	e basic p	roperties	of Penly	concrete
Heating temperature [°C]	25	200	400	600	800
Moisture content at saturation [% kg/kg]	4.8	5.2	5.6	7.5	8.6
Dry density [kg/m <sup>3</sup> ]	2290	2290	2275	2260	2200
(b) Effect of heating temperature	re on the	basic pro	perties o	f Temelii	n concrete
Heating temperature [°C]	25	200	400	600	800
Moisture content at saturation [% kg/kg]	7.0	7.0	7.3	8.8	9.8
Dry density [kg/m <sup>3</sup> ]	2206	2206	2193	2172	2156

concrete, the Ca(OH)<sub>2</sub> production after heating to more than 460°C should be lower. This assumption is supported by a lower density decrease of Penly concrete than of Temelin concrete between 400°C and 600°C as shown in Table 4a,b. Therefore, a logical conclusion is that the significant increase of porosity at about 500°C was caused mostly by crack appearance at the matrix/aggregate interface and partially also in the aggregates themselves due to the local overpressure.

In order to prove this statement, we have done visual observations, at first. We realized that on the specimens of Penly concrete most of the pebbles appeared cracked or split after being exposed to the temperatures higher than 400-500°C, and well visible cracks  $\sim$  500 µm wide were also observed at the matrix/aggregate interfaces. The evolution of thermal cracks at elevated temperatures is documented in Fig. 8a-d. The specimens shown here were exposed to elevated temperatures at 200°C, 400°C, 600°C, and 800°C, isothermal dwells were always 1 h. From Fig. 8a-d it is evident that the main reason for crack formation is the low quality of aggregates in Penly concrete, which consists of submicrocrystalline silicon dioxide, like chalcedony and opal, and limestone, mainly chalks with 90–99% of CaCO<sub>3</sub> and microfossiliferous covering. Some aggregates are composed of clay limestone with ferrous hydroxides, which are oxidized at elevated temperature to stable  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

Siliceous and calcareous aggregates were further analyzed by differential thermal analysis (DTA) and thermogravimetry (Figs. 9a,b and 10a,b). We can observe that the chalk starts to decompose at 782°C, the weight loss is 43.83%, which means that the chalk is an almost pure calcium carbonate. Carbon dioxide leaks from aggregates and causes deterioration of cement stone, because 1 kg of this chalk involves 438.33 g of CO<sub>2</sub>. The siliceous compounds are decomposed during an exposure to a temperature of at least 580°C. The weight loss of 3.20% is attributed to leakage of water vapor from the microporous system of opal. Further reason for the crack formation is the thermal decomposition of very small limestone grains in cement stone at 755°C, see Fig. 11a,b. These grains are apparently identical with the calcareous filler in the mixture, and their effect can also be illustrated by a significant decrease of dry density of Penly concrete between 600°C and 800°C (see Table 4a).



Fig. 8. Digital photographs of the Penly concrete specimens exposed to different temperatures: (a)  $200^{\circ}$ C for 1 h, (b) 1 h at  $200^{\circ}$ C and 1 h at  $400^{\circ}$ C, (c) 1 h at  $200^{\circ}$ C,  $400^{\circ}$ C and  $600^{\circ}$ C, and (d) 1 h at  $200^{\circ}$ C,  $400^{\circ}$ C,  $600^{\circ}$ C and  $800^{\circ}$ C.



Fig. 9. (a) DTA of siliceous aggregates of Penly concrete. (b) Thermogravimetry of siliceous aggregates of Penly concrete.

The crack formation is always accompanied by substantial strength lowering, and appearance of wider cracks leads logically to a more dramatic decrease of the strength of a material. In this respect our observations are in a very good agreement with the results of Felicetti et al. [22] who have found the residual compressive strength of Penly concrete to decrease under 35% of its original value after heating to 400°C, and under 10% for 500°C.

For the sake of comparison of the effect of high temperatures on both types of concrete investigated throughout this paper, the cracks in Temelin concrete appeared in the cement binder only, no visible cracks were observed in the



Fig. 10. (a) DTA of chalk in Penly concrete. (b) Thermogravimetry of chalk in Penly concrete.

aggregates. The quality of aggregates was therefore apparently much better than in Penly concrete.

The lower-quality aggregates in the Penly concrete were probably also responsible for the differences in moisture diffusivity of both materials induced by the frost cycles (Fig. 7). Table 5a shows that the moisture content at saturation of Penly concrete increased by 10% after only 200 cycles and by additional about 10% after another 100 cycles. The dry density decreased by about 2% after 300 cycles, which is again an illustration of substantial deterioration processes taking place in the material.

On the other hand, the dry density of Temelin concrete remained unchanged even after 400 cycles, and the saturation moisture content increase did not begin before 200 cycles. This supports well our hypothesis that the quality of aggregates played a decisive role for the durability of the studied materials. We have good reasons to conclude that the relatively slow increase of moisture diffusivity observed for Temelin concrete was related mostly to the aging of the cement binder, and its aggregates remained practically unaffected by the frost cycling process. Also in this case, our observations were in good agreement with the measurements of bending strength done by Trtik and Vodička [23].

Comparing the results of  $\kappa$  measurements in Figs. 3 and 7, we can observe that the values of moisture diffusivity of both Temelin and Penly concrete measured on the 6-monthold specimens (i.e., just after their delivery, Figs. 3 and 5) were about two times lower than those that were measured



Fig. 11. (a) DTA of cement stone of Penly concrete. (b) Thermogravimetry of cement stone of Penly concrete.

Table 5

(a)	Effect	of the	number	of frost	cycles	on	the	basic	properties	of Penl	y
cor	ncrete										
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Number of frost cycles	0	200	300
Moisture content at saturation	4.8	5.2	5.5
[% kg/kg] Dry density [kg/m <sup>3</sup> ]	2290	2262	2246

(b) Effect of the number of frost cycles on the basic properties of Temelin concrete

Number of frost cycles	0	200	400	
Moisture content at saturation	7.0	7.0	7.6	
[% kg/kg]				
Dry density [kg/m <sup>3</sup> ]	2209	2209	2209	

on the specimens left for additional 10 months in water (reference specimens for the frost cycling procedure). The main reason of this fact is probably the "natural" aging of both materials. As the observed changes for both materials were about the same, we believe that the aggregates did not play any significant role in this case.

We compared the results of our water suction tests with the results obtained by other researchers in the past. First, we compared the water absorption coefficients measured on uncracked concrete. As most of the authors did not use the basic SI units, we had to recalculate their data to obtain comparable numbers. Sabir et al. [24] obtained for cement mortar A = 0.028 kg m<sup>-2</sup> s<sup>-1/2</sup>. Krus et al. [25] measured for cement pastes with various water to cement ratios and various admixtures A = 0.0016 - 0.033 kg m<sup>-2</sup> s<sup>-1/2</sup>. Martys and Ferraris [26] obtained for conventional concrete bench dried A=0.0085 kg m<sup>-2</sup> s<sup>-1/2</sup>, for high-performance concrete bench dried A = 0.0041 kg m<sup>-2</sup> s<sup>-1/2</sup>. From the water suction data in our previous experiments on cement mortar [27] we calculated A = 0.025 kg m<sup>-2</sup> s  $^{-1/2}$ . All these results are difficult to be compared exactly between each other because the water absorption coefficients depend highly on the water to cement ratio and on the admixtures as it has been demonstrated in Ref. [25], and also the aggregate size is an important factor. Our previous results on cement mortar [27] can be seriously compared only with those in Ref. [24]. The difference of about 10% between the two results can be considered reasonable. Therefore, we can conclude that our water suction experimental setup meets the basic requirements for the necessary precision. Comparing our results on uncracked specimens with those given above shows that our two high-performance concretes exhibited significantly higher values of water absorption coefficients than those measured in Ref. [26], but it should be taken into account that our measurements were done 6 months after the specimen production while those in Ref. [26] just after 28 days. The results in Tables 2a,b and 3a,b have shown that the increase of the water absorption coefficients of both Penly and Temelin concretes due to the natural aging was remarkable, it was about 50% during a 10-month period. Therefore, we can also conclude here that the difference compared to the Penly

concrete is not very high. However, the same statement cannot be given concerning the Temelin concrete that had almost two times higher water absorption coefficient than the Penly concrete. Here the measured results were closer to the data on cement mortar in Refs. [24,27] than to the data on high-performance concrete in Ref. [26].

Due to the difficulties in generating desirable crack patterns in concrete specimens and availability of appropriate methods for concrete permeability measurements, a limited number of studies have been done on the permeability of cracked concrete. For instance, Bažant et al. [28] predicted a several orders of magnitude increase in water permeability for the crack width over 0.2 mm, Wang et al. [29] and later Aldea et al. [30] observed an up to seven orders of magnitude increase in water permeability for tensile stress-induced cracks up to 400 µm wide. These results are unfortunately not exactly comparable with our results because the water retention curves of concrete in these experiments were not given, and not water absorption tests but only permeability tests were performed. Reinhardt et al. [31] have measured penetration of various fluids into cracked and repaired concrete but they were interested in the penetration depths only and the data on cumulative water absorption were not given. In addition, the main investigated fluids were acetone and *n*-heptane, not water. Therefore, here we also cannot arrive at an exact comparison with our data. We can give qualitative statements only, not the quantitative ones.

Thermal cracks are naturally not that regular or equally spaced as those induced by tensile stress, and the main water flow goes through only several wide cracks, i.e., only several preferential ways appear. This was clearly demonstrated in our experiments where Penly concrete exposed to temperatures 600°C and higher had one order of magnitude higher moisture diffusivity than Temelin concrete, although its global porosity and saturation moisture content remained still lower. Nevertheless, certain analogy of water transport in thermally and mechanically cracked concrete exists, and the mechanisms of water transport are similar.

As mentioned before, water permeability and moisture diffusivity are easily convertible quantities if one knows the water retention curve of a given material. Our approximate method for determination of moisture diffusivity is very fast (the measurement takes only several hours) while still retaining a reasonable precision as has been shown before [18]. This is in our opinion its very favorable feature because comparable measurements of water permeability of concrete [29] take 20–50 days.

## 6. Conclusions

The experimental work in this paper have shown that the main reason for the observed significant increase in moisture diffusivities of both high-performance concretes after being exposed to high temperatures or frost cycles was the appearance of cracks allowing fast water penetration into the material specimens.

From the qualitative point of view, this corresponds well to the theoretical predictions of the effects of high temperatures on concrete. The production of gaseous substances accompanying the decomposition of calcium hydroxide and calcium silicate hydrates after high temperature exposure leads to local overpressure in the porous system and subsequent crack formation. The theoretical predictions of consequences of cyclic freezing and thawing are also in general accordance with our measured results. The density difference between water and ice leads to an internal stress increase in the porous system in the freezing period that may result in the deterioration of the microstructure of the porous matrix.

However, from the quantitative point of view, the response of both concretes to the high temperature exposure and freeze/thaw cycles was quite different. The Penly concrete, which was in normal conditions of better quality than Temelin concrete because it contained better cement and had lower porosity, resisted high temperatures and frost cycles much worse. This allows us certain generalization.

We can conclude that the quality of aggregates plays a more important role for the concrete durability in both high temperature conditions and in the conditions of cyclic freezing and thawing than the quality of cement.

The calcareous aggregates should be avoided in concrete with presumed high temperature exposure, as well as any calcareous fillers, because their thermal decomposition accompanied by release of substantial amount of carbon dioxide can damage the internal microstructure of the matrix due to the increase of internal pressure. Also, the presence of opal in aggregates is not suitable because its microporous system contains water, which can evaporate and damage the porous matrix. Fully quartzitic aggregates perform much better in high temperature conditions.

High quality siliceous aggregates with very low porosity and very good mechanical properties are also the most proper solution for concrete supposedly exposed to freeze/ thaw cycles. The siliceous aggregates with higher porosity such as opal are more sensitive to water freezing in the porous system because they contain a higher amount of water in natural conditions, and the stress increase after freezing is higher than in low porosity aggregates. The calcareous aggregates have significantly worse mechanical properties than quartzitic aggregates, and therefore also their resistance to water freezing resulting in significant internal stress increase in the porous system is worse.

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